

## BRIEF COMMUNICATION

# The First Organically Templated Layered Cobalt Phosphates: Hydrothermal Syntheses and Crystal Structures of $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$ and $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$

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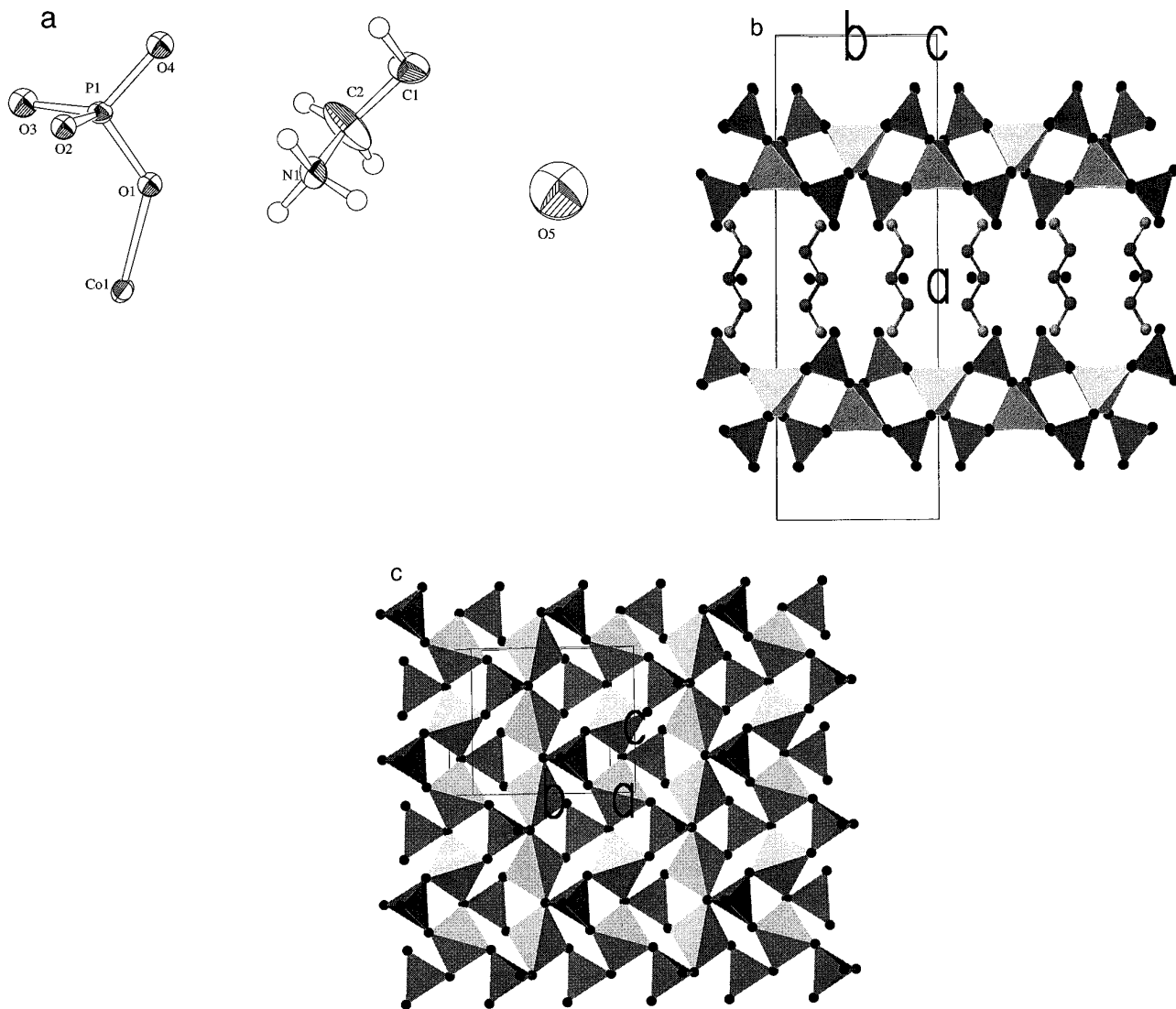
The first organically templated layered cobalt phosphates have been prepared and structurally characterized by single crystal X-ray diffraction. The layered cobalt phosphate  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**) was prepared hydrothermally at 170°C over 48 h from an aqueous solution of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 1,3-diaminopropane,  $\text{H}_3\text{PO}_4$  (85%), and  $\text{H}_2\text{O}$  in the mole ratio 1:7.2:4:444. Phosphate **2**,  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$ , was prepared in an analogous fashion from a mixture of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , 1,4-diaminobutane,  $\text{H}_3\text{PO}_4$  (85%),  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$ , and  $\text{H}_2\text{O}$  in the mole ratio 1:4:3.5:3:444 heated at 170°C for 47 h, to give brilliant blue plates in 70% yield. Crystal data for  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**): orthorhombic  $Cmc2_1$ ,  $a = 22.663(3)$  Å,  $b = 7.6255(8)$  Å,  $c = 6.7676(7)$  Å,  $V = 1174.7(6)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 2.273$  g cm<sup>-3</sup>; structure solution and refinement based on 507 reflections with  $I_0 \geq 3\sigma(I_0)$  (MoK $\alpha$  radiation,  $\lambda = 0.71073$  Å) converged at  $R = 0.030$ . Crystal data for  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**2**): monoclinic  $P2_1/a$ ,  $a = 7.508(3)$  Å,  $b = 23.655(4)$  Å,  $c = 6.775(1)$  Å,  $\beta = 90.55(2)^\circ$ ,  $V = 1203.3(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 2.185$  g cm<sup>-3</sup>; structure solution and refinement based on 1305 reflections with  $I_0 \geq 3\sigma(I_0)$  (MoK $\alpha$ ,  $\lambda = 0.71073$  Å) converged at  $R = 0.048$ . Magnetization measurements indicate that **2** orders to a weak ferromagnetic state near 25 K. © 1996 Academic Press, Inc.

The dramatic expansion of the chemistry of metal phosphate phases reflects their applications to heterogeneous catalysis (**1**, **2**) and as sorbents and ion exchangers (**3**). Vanadium phosphate phases have been extensively studied since the report of their effectiveness as catalysts for the selective oxidation of butane to maleic anhydride (**4**). Likewise, the ion exchange properties of Group IV and Group V phosphates have received intense attention (**3**), and considerable progress has been reported in the development

of zinc (**5**), oxomolybdenum (**6**), and vanadium phosphate (**7**) phases. While several members of the class of inorganic cobalt phosphates have been described (**8**–**13**), examples of organically templated layered or zeolitic cobalt phosphate phases remain rare. One notable exception is  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**14**), a material exhibiting a three-dimensional framework of corner-sharing tetrahedra.

Since the use of structure-directing organic molecules has evolved into a successful strategy for the synthesis of layered and zeolitic materials, we sought to expand the cobalt phosphate family of solids by exploiting the introduction of various organoammonium cations as templates in the hydrothermal preparation of the solids. We report here the syntheses and structural characterizations of the first examples of layered cobalt phosphate phases containing organic templates,  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**) and  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**2**). While both **1** and **2** possess layers of identical structure, which are constructed from one-dimensional (1-D) chains of corner-sharing cobalt tetrahedra connected by phosphorus tetrahedra, it is noteworthy that the identity of the template influences the alignment of  $\{\text{Co}(\text{PO}_4)\}$  layers in the solid.

The layered cobalt phosphate  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**) was prepared hydrothermally at 170°C over 48 h from an aqueous solution of  $\text{CoCl}_2$ , 1,3-diaminopropane,  $\text{H}_3\text{PO}_4$  (85%), and  $\text{H}_2\text{O}$  in the mole ratio 1:7.2:4:444 in a polytetrafluoroethylene-lined 23 ml acid digestion bomb at 35% fill volume. The product **1** was isolated as bright blue plates mixed with an amorphous pink solid (Yield ca. 30%). Phosphate **2**,  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$ , was prepared in an analogous fashion



**FIG. 1.** (a) The atoms of the asymmetric unit of  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**), showing the atom-labeling scheme and 50% thermal ellipsoids. (b) A view of the structure  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**), parallel to the crystallographic **b** axis. The cobalt phosphate layers are represented by corner-sharing  $\{\text{CoO}_4\}$  and  $\{\text{PO}_4\}$  tetrahedra and the organic cations by a ball and stick representation. (c) A view of the structure parallel to the **a** axis, showing the linear  $\{\text{Co}-\text{O}-\text{Co}-\text{O}-\}$  chains of corner-sharing Co tetrahedra.

from a mixture of  $\text{CoCl}_2$ , 1,4 diaminobutane,  $\text{H}_3\text{PO}_4$  (85%),  $(n\text{-C}_4\text{H}_9)_4\text{NOH}$ , and  $\text{H}_2\text{O}$  in the mole ratio 1 : 4 : 3.5 : 3 : 444 heated at  $170^\circ\text{C}$  for 47 h, to give brilliant blue plates in 70% yield.

As shown in Fig. 1b, the structure of **1** consists of inorganic Co–O–P layers with the propanediammonium cations and the  $\text{H}_2\text{O}$  of crystallization occupying the interlamellar regions.<sup>1</sup> The Co(II) sites exhibit tetrahedral coordination geometry, through bonding to oxygen donors of each of four adjacent phosphate tetrahedra. Two adjacent cobalt tetrahedra share a common vertex with a phosphate group, to generate a linear chain of corner-sharing Co(II)

<sup>1</sup> For both structures **1** and **2**, data were collected on a Rigaku AFC7R diffractometer with graphite nonchoromated  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and an 18 kW rotating anode generator. The data were collected at a temperature of  $20 \pm 1^\circ\text{C}$  using the  $\omega$ - $2\theta$  scan technique to  $60.1^\circ$  in  $2\theta$  at a scan speed of  $16.0^\circ/\text{min}$  (in  $\omega$ ). The intensities of three standard reflections were measured after every 150 reflections. Empirical absorption corrections and corrections for Lorentz and polarization effects were applied in the usual manner (7). The structures were solved by direct methods. Structure solutions and refinements were performed as previously described (7). Crystal data for  $[\text{H}_3\text{N}(\text{CH}_2)_3\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)] \cdot 0.5\text{H}_2\text{O}$  (**1**): orthorhombic  $Cmc2_1$ ,  $a = 22.663(3) \text{ \AA}$ ,  $b = 7.6255(8) \text{ \AA}$ ,  $c = 6.7676(7) \text{ \AA}$ ,  $V = 1174.7(6) \text{ \AA}^3$ ,  $Z = 8$ ,  $d_{\text{calc}} = 2.273 \text{ g cm}^{-3}$ ; structure solution and refinement based on 507 reflections with  $I_0 \geq 3\sigma(I_0)$  ( $\text{MoK}\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ) converged at  $R = 0.030$ .

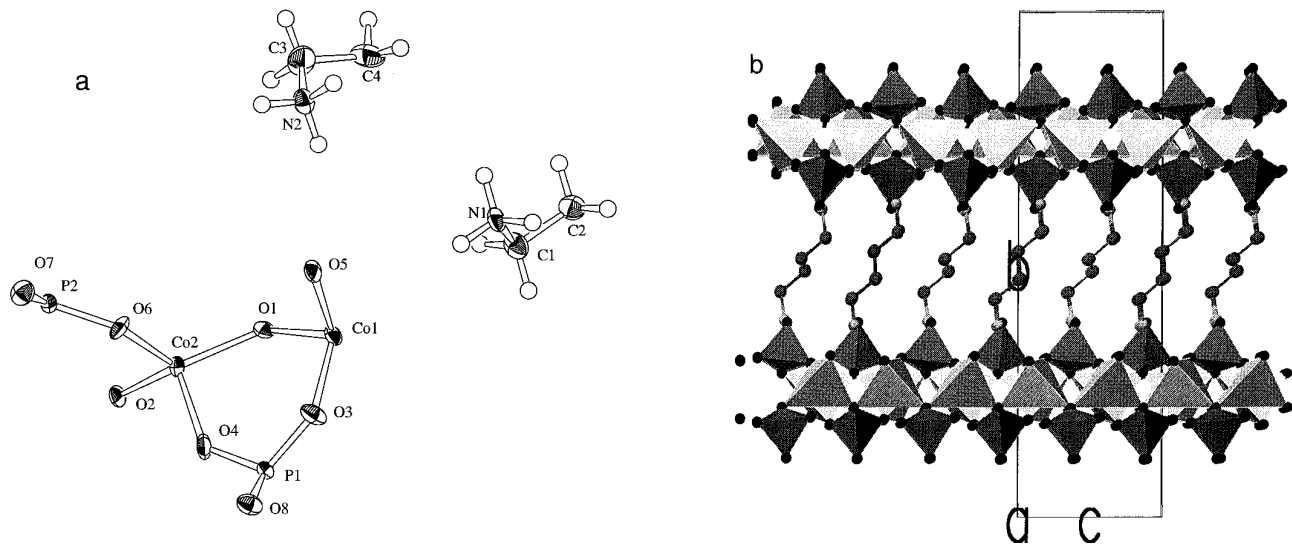


FIG. 2. (a) The asymmetric unit of **2**, showing the atom-labeling scheme and 50% thermal ellipsoids. (b) A view of the structure of **2**, parallel to the crystallographic **a** axis.

tetrahedra which runs parallel to [001], as shown in Fig. 1c. Neighboring cobalt chains are linked through phosphate tetrahedra, such that each phosphate group utilizes one oxygen donor to bridge adjacent Co(II) sites of a chain and two oxygen donors to bridge to each of two Co(II) sites on a neighboring chain, as shown in Fig. 1c. Each phosphate unit projects a pendant {P=O} group into the interlamellar region, in an alternating pattern above and below the plane.

The Co(II) sites of cobalt phosphate phases generally adopt five or six coordination (8–11). In those cases where tetrahedral geometry is observed (12, 13), the Co/P ratio is not unity, except for the three-dimensional framework structure of  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**14**). It is curious that an additional methylene group in the template of **1** should result in a 2-D network rather than the 3-D framework adopted for the ethylenediammonium species. Consequently, compound **1** represents the first example of an organically templated 2-D cobalt phosphate. It is also noteworthy that while the Co–O bond distances in  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  are essentially equivalent and average 1.95 Å, for **1** there are three Co–O distances averaging 1.95(2) Å, while the third is 2.03(2) Å. This latter distance reflects the unsymmetrically bridging, three coordinate phosphate oxygen linking two Co(II) sites of the linear chains in **1**. In contrast, the 3-D framework of  $[\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  consists of isolated {CoO<sub>4</sub>} tetrahedra, that is, there are no {Co–O–Co} linkages or pendant {P=O} units. There are three distinct {P–O} distances in **1**, consistent the bonding mode adopted: the {P–O} distance for the  $\mu_2$ -bridging type is 1.578(4) Å; those for the two oxygen donors adopting the symmetrically

bridging mode exhibit an average {P–O} distance of 1.54(1) Å, and the pendant {P=O} group is relatively short at 1.506(5) Å.

As illustrated in Fig. 1b, the Co–O–P layers in **1** are three polyhedra in thickness as a consequence of the projection of the pendant apices of the phosphate tetrahedra above and below the planes. The interlamellar repeat distance is 11.33 Å. The organic cations are hydrogen-bonded to the oxygen atoms of the framework, with particularly strong interactions with the pendant {P=O} groups. The organic template directs an –NH<sub>3</sub><sup>+</sup> group into the cavity between neighboring {P=O} groups of the layers, with the N ··· N vectors of the templates aligned at an angle of 90° with the inorganic plane. The planes are stacked in perfect registry with {P=O} groups of neighboring planes pointing directly at one another.

The structural consequences of template modifications are dramatically illustrated by the structure of  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**2**), shown in Fig. 2.<sup>2</sup> The polyhedral connectivity within the inorganic layer of **2** is identical to that of **1**. Similarly, the metrical parameters are essentially unchanged. In fact, the interlamellar spacing for **2** is ca. 11.8 Å, compared to 11.3 Å for **1**. Consequently, the template cannot orient with the N ··· N vector perpen-

<sup>2</sup> Crystal data for  $[\text{H}_3\text{N}(\text{CH}_2)_4\text{NH}_3]_{0.5}[\text{Co}(\text{PO}_4)]$  (**2**): monoclinic  $P2_1/a$ ,  $a = 7.508(3)$  Å,  $b = 23.655(4)$  Å,  $c = 6.775(1)$  Å,  $\beta = 90.55(2)^\circ$ ,  $V = 1203.3(5)$  Å<sup>3</sup>,  $Z = 8$ ,  $d_{\text{calc}} = 2.185$  g cm<sup>-3</sup>; structure solution and refinement based on 1305 reflections with  $I_0 \geq 3\sigma(I_0)$  (MoK $\alpha$ ,  $\lambda = 0.71073$  Å) converged at  $R = 0.048$ . Atomic coordinates, bond lengths and angles, and thermal parameters for **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Linsfield Road, Cambridge CB2 1EW, UK.

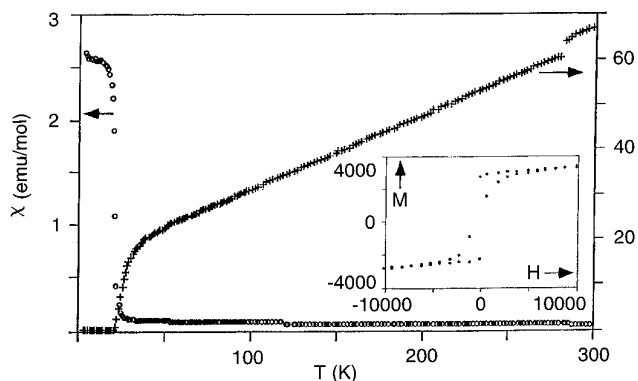


FIG. 3. Temperature dependence of  $\chi$  and  $\chi^{-1}$ , as well as the variation in  $M(H)$  (inset) for **2** indicating the onset of the weak ferromagnetism at ca. 25 K.

dicular to the planes but must tilt the  $N \cdots N$  axis ca.  $15^\circ$  from the vertical. Since the  $-\text{NH}_3^+$  termini of the templates adopt the same orientation with respect to the pendant  $\{\text{P}=\text{O}\}$  groups of neighboring planes in both structures, this necessitates the shearing of planes along the crystallographic  $ac$  plane of **2**, such that the  $\{\text{P}=\text{O}\}$  of neighboring planes of **2** no longer point directly at one another as in **1**, but rather at the midpoint of the “trough” between  $\{\text{P}=\text{O}\}$  arms. In this fashion, variation in the template results in modifications not only of the interplanar spacings but also of the registry of planes. It is noteworthy that the layer structure of **1** and **2** is quite distinct from that observed for the 2-D cobalt-phosphite phase  $\text{Co}(\text{HPO}_3)(\text{H}_2\text{O})$ , which consists of zig-zag chains of edge-sharing  $\{\text{CoO}_6\}$  octahedra linked through phosphite bridges (15).

The variable temperature magnetic susceptibility for **2** is shown in Fig. 3. The linear behavior of  $\chi^{-1}(T)$  for  $T > 75$  K is indicative of paramagnetism as is the room temperature  $\mu_{\text{eff}}$  of  $5.40 \mu_{\text{B}}$ , which, while significantly larger than the spin-only value of  $3.88 \mu_{\text{B}}$ , is consistent with experimentally observed moments for  $\text{Co}(\text{II})$  complexes (16). The large negative  $\theta = -86$  K results from the substantial antiferromagnetic interactions present. At ca. 25 K, **2** appears to undergo a transition to a weak ferromagnetic state (Fig. 3) as suggested by the characteristic increase in  $\chi$  upon cooling through 25 K and the obser-

vation of hysteresis loops in the  $M(H)$  variation below the critical temperature (Fig. 3, inset). This state likely results from the ordering of the moments generated from the pairwise canted antiferromagnetic interactions between neighboring corner-sharing  $\text{CoO}_4$  tetrahedra in the 1-D chain.

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